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(54) **Phosphate treatment solution for composite structures and method for treatment.**

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EP-A- 0 264 811
FR-A- 2 159 181

PATENT ABSTRACTS OF JAPAN, vol. 13, no. 21 (C-560)[3369], 18th January 1989; & JP-A-63 223 186 (NIPPON PARKERIZING CO., LTD) 16-09-1988

CHEMICAL ABSTRACTS, vol. 104, no. 12, 24th March 1986, page 301, abstract no. 93350t, Columbus, Ohio, US; & JP-A-60 204 889 (NISSHIN STEEL CO., LTD) 16-10-1985

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Description**BACKGROUND OF THE INVENTION**5 (i) Field of the Invention

The present invention relates to a phosphate treatment solution for treating the surfaces of automobile bodies constituted of the combination of steel plates and other materials such as zinc and aluminum, i.e., the composite structures, and it also relates to a method for the treatment.

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(ii) Description of the Prior Art

Heretofore, when an automobile body containing aluminum materials as constitutional parts is treated with a phosphate solution, the aluminum parts are first subjected to a chromate treatment mainly to heighten performance, and the thus treated aluminum parts are then assembled to the automobile body comprising steel plates and zinc-plated steel plates. Afterwards, the phosphate treatment is carried out, followed by a cathodic electrodeposition coating. According to this known technique, chromium and aluminum are partly dissolved out from the first formed chromate coating on the aluminum parts in the subsequent phosphate treatment step, so that the chromate coating tends to become imperfect, and thus the phosphate coating is not formed, either.

In the above-mentioned technique, the aluminum parts are subjected to the chromate treatment prior to assembling these aluminum parts to the automobile as described above, and therefore chromium and aluminum are dissolved out in the subsequent phosphate treatment step, so that the chromate coating and the phosphate coating become imperfect. In consequence, when a paint coating is subsequently carried out, the resulting paint film is poor in adhesive performance, and in particular, there is a problem that the secondary adhesion after water-soaking (hereinafter, wet adhesion) is poor.

In the manufacturing process of the automobile bodies, a parts assembly, a pretreatment and a paint coating are carried out in this order, and in the conventional process, the aluminum parts are separately treated by another procedure. That is, the aluminum parts are subjected to a water-rinsing, a chromate treatment and a water-rinsing/drying in this order, and further subjected to the above-mentioned assembly, the pretreatment and the paint coating. Therefore, there is also the problem that operating efficiency is bad and costs are high.

In the case that the aluminum parts are assembled to the automobile body without performing any chromate treatment and then subjected to the phosphate treatment, the conventional known treatment solution cannot provide any phosphate coating having satisfactory performance, i.e., excellent filiform corrosion resistance and wet adhesion, on the surfaces of the aluminum parts. After all, a poor coating is merely formed which is unsuitable for the automobile bodies where the high paint film performance is required. In addition, aluminum ions are dissolved into the phosphate treatment solution in this treatment step, and inconveniently, these aluminum ions have a bad influence on the phosphate coating on the surfaces of other materials in the automobile body.

The French patent application FR-A-2 159 181 relates to an acidic free acidity of 0.2 to 5 points phosphate treatment solution for the treatment of structural parts having a constitution of aluminium, iron and zinc, which comprises ions of zinc, phosphate, nitrate, nitrite, fluoride, sodium and potassium.

45 **SUMMARY OF THE INVENTION**

The present invention has been achieved to solve the above-mentioned conventional various problems.

An object of the present invention is to provide an improved phosphate treatment solution for composite structures.

Another object of the present invention is to provide an efficient method for the treatment of composite structures.

The first feature of the present invention is directed to a phosphate treatment solution for composite structures which is characterized by containing 0.3-2.0 g/l of zinc ions, 0.3-4.0 g/l of nickel ions, 0.3-2.0 g/l of manganese ions, 3-10 g/l of sodium ions, 0.1-10 g/l of potassium ions, 5.0-25.0 g/l of phosphate ions, 0.11-7.0 g/l of total fluorine ions, 4.0 g/l or more of nitrate ions and 0.01-1.0 g/l of nitrite ions as main components, the aforesaid treatment solution having a pH-value of 2.0-3.5, the aforesaid total fluorine ions being composed of complex fluorine ions in 0.1-5 g/l as fluorine and free fluoride ions in 0.01-2 g/l.

The second feature of the present invention is directed to a method for treating composite structures which is characterized by using the above-mentioned treatment solution and a mixture of sodium bifluoride and potassium bifluoride as an additive liquid, while the concentration of the free fluoride ions is maintained.

The present invention can be applied to a conventional manufacturing procedure without changing it, and even in this case, an excellent phosphate coating can be formed on the surfaces of the composite structures as a basecoat for cathodic electrodeposition coating.

When the content of the aluminum ions in the treatment solution increases up to a level of 400 ppm or more with use, the concentration of the free fluoride ions should be maintained at 0.01-2 g/l, whereby that of the total fluorine ions is controlled to be in the range of 0.11-7.0 g/l.

DETAILED DESCRIPTION OF THE INVENTION

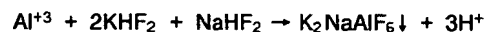
For composite structures comprising different materials such as aluminum, steel and galvanized steel (including zinc alloy plated, galvanized etc.), a phosphate treatment is simultaneously possible, if the following requirements are met:

(1) The resulting paint films on all the different materials being excellent in the performance.

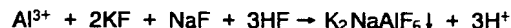
(2) The concentration of aluminum ions being controlled sufficiently. Because if not controlled, aluminum is dissolved into a phosphate treatment solution during the treatment, so that the aluminum ions are accumulated and thereby impede the formation of the phosphate coating and deteriorate the performance of the coating.

Therefore, it is essential for the present invention that the total fluorine ions present in the treatment solution are composed of 0.1-5 g/l of complex fluorine ions and 0.01-2 g/l of free fluoride ions. When the composite structures are immersed in the treatment solution at 30-55°C for 1-5 minutes in accordance with the present invention in order to form a zinc phosphate coating on the surfaces of the structures, said coating contains 1-10% (preferably about 4%) of each of nickel and manganese.

The aluminum ions, which are dissolved into the treatment solution and then gradually accumulated therein, prevent the formation of the phosphate coating on steel plates and aluminum surfaces of the composite structures. In particular, when the content of the aluminum ions is 150 ppm or more, the formation of the phosphate coating is extremely poor. Therefore, it is preferred that the content of the aluminum ions is maintained in the range of 0 to less than 150 ppm. Accordingly, in the continuous treatment by the use of the treatment solution, KHF_2 and NaHF_2 are suitably added in an amount corresponding to the amount of the dissolved aluminum ions in accordance with the formula



in order to maintain the concentration of the free fluoride ions during the treatment in a predetermined range and to control the concentration of the dissolved aluminum ions, whereby a proper phosphate coating can be formed on the surfaces of the composite structures. It should be noted here that the same effect can be obtained by means of adding NaF, KF and HF as can be seen from the following reaction formula:



In this case, the concentration of the aluminum ions is controlled by adjusting the concentration of the free fluoride ions during the treatment in the solution, and this control is accomplished by adding KHF_2 and NaHF_2 thereto in order to precipitate the aluminum ions in the form of K_2NaAlF_6 . It is important that these fluorides are not used separately but as a mixture of the sodium bifluoride and the potassium bifluoride in a ratio of one molecule of the former:two molecules of the latter, and this mixture can be added to the treatment solution continuously or intermittently. Such a procedure permits instantaneous formation of a precipitate of the aluminum compound, accurate measurement of the concentration of the free fluoride ions, and easy control of the concentration of the aluminum ions. In this case, the mixture of the above-mentioned fluorides may be liquid or solid.

When the phosphate treatment solution of the present invention is used, the following characteristics can be perceived: On an iron material and a zinc-plated material of the composite structures, there is formed a phosphate coating which is substantially comparable to what is formed by an usual phosphate treatment, and on an aluminum material, there is formed a coating having a noticeably high performance. That is, on the aluminum surface, the phosphate coating of $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ can usually be formed, even when three components of phosphoric acid, hydrofluoric acid and zinc are used. However, in the present invention, nickel and manganese are each additionally present in a ratio of 1 to 10% in the phosphate

coating as described above, and therefore the coating crystals are densified and the wet adhesion and the outdoor exposure performance are improved.

The phosphate coatings formed by using the treatment solution of the present invention were compared with a conventional phosphate coating after finish-paint. The results are set forth in Table 1.

Table 1
(comparison of coatings after finish-paint)

	Coating Weight	Ni in the Coating	Mn in the Coating	Blister Width after Exposed for 1 year	Wet Adhesion*
Zn-Phosphate Type of Conventional Example	1.0 g/m ²	0%	0%	15 mm	28/100
Chromate Type of Conventional Example	-	-	-	3 mm	95/100
Present Invention	1.0 g/m ²	15%	36%	1 mm	100/100

* Please refer to the Table 2.

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Zn	1.2 g/l
Na	7.0 g/l
PO ₄	15 g/l
NO ₃	7 g/l
SiF ₆	3 g/l
NO ₂	0.5 g/l
pH	3.2

10 Composition of conventional chromate treatment solution

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CrO ₄	7 g/l
PO ₄	10 g/l
F	2 g/l
pH	1.5

Composition of treatment solution of the present invention

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Zn ²⁺	1.4 g/l
Ni ²⁺	1.5 g/l
Mn ²⁺	0.5 g/l
PO ₄ ⁻³	15.5 g/l
SiF ₆ ⁻²	3 g/l
F ⁻	100 ppm
NO ₃ ⁻	7 g/l
K ⁺	0.5 g/l
Na ⁺	7 g/l
NO ₂ ⁻	0.2 g/l
pH	3.2

A treatment solution and a treatment method of the present invention will be described in detail in reference to an example, and the effect of the present invention will also be elucidated by comparing with conventional examples.

Example 1

(1) Composition of treatment solution

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Zn ²⁺	1.1-1.2 g/l
Ni ²⁺	0.9-1.0 g/l
Mn ²⁺	0.4-0.6 g/l
PO ₄ ³⁻	15.0-15.5 g/l
SiF ₆ ²⁻	2-3 g/l
free F ⁻	0.08-0.15 g/l
NO ₃ ⁻	6-8 g/l
K ⁺	0.05-0.5 g/l
Na ⁺	6.8-7.8 g/l
NO ₂ ⁻	0.15-0.25 g/l
pH	3.2-3.3

(2) Treatment conditions

Immersion at 45° C for 2 minutes

5 Under the above-mentioned conditions, an automobile body comprising an aluminum plate of #5000 type, an electrogalvanized steel plate, a zinc-nickel-plated steel plate and a steel plate (Fe:Al:Zn-Ni = 6:1:3) was immersed in the above-mentioned treatment solution in a ratio of 2 m²/l, while the concentration of free fluoride was measured and adjusted during the treatment so as to be in the controlled range [free fluoride ions during the treatment = (amount of total fluorine) - (fluorine content in complex fluorine) - (F in AlF₃)],
10 while a 5% mixed aqueous solution of a KHF₂ powder having a water content of 10% and NaHF₂ flakes in a ratio of two molecules:one molecule was added thereto, and while a replenishing solution was also added thereto so as to maintain concentrations of other components. Afterward, the performance of each specimen was measured. The results are set forth in Table 2.

15 Comparative Example 1

The same procedure as in Example 1 was repeated with the exception that the mixed solution of KHF₂ and NaHF₂ was replaced by 5% NaHF₂. The results are set forth in Table 2.

20 Comparative Example 2

The same procedure as in Example 1 was repeated with the exception that the concentration of free fluoride was maintained at about 0 g/l. The results are set forth in Table 2.

In this case, piping systems are more liable to clog than in Example 1.

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Comparative Example 3

The same procedure as in Example 1 was repeated with the exception that the mixed solution of KHF₂ and NaHF₂ was replaced by a 5% KHF₂ solution. The results are set forth in Table 2.

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Comparative Example 4

The same procedure as in Example 1 was conducted except that Mn²⁺ was eliminated from the treatment solution.

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Comparative Example 5

The same procedure as in Example 1 was conducted except that Ni²⁺ was eliminated from the treatment solution.

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Table 2

5	Test Item	Plate for Test	Example 1
10	Wet Adhesion*	Aluminum Plate Zinc-plated Steel Plate Steel Plate	100/100 100/100 100/100
15	Outdoor Exposure Performace*	Aluminum Plate Zinc-plated Steel Plate Steel Plate	1 mm 3 mm 10 mm
20	Al ³⁺ in Treatment Solution		5 ppm
	Coating Weight	Aluminum Plate	1.2 g/m ²
25	Ni in the Coating	Aluminum Plate	17 mg/m ²
	Mn in the Coating	Aluminum Plate	36 mg/m ²

30 * Painting Conditions:
 Cathodic Electrodeposition + Baking at 175°C for
 20 min. + Intercoating + Topcoating
 Cathodic Electrodeposition: Power Top U-100 made by
 35 Nippon Paint Co., Ltd.; 20 µm
 Intercoating: KPX36 made by Kansai Paint Co., Ltd.;
 30-35 µm
 Topcoating: Acrylic type. White, made by Kansai Paint
 Co., Ltd.; 30 µm

40 * Wet Adhesion Test:
 Test panels with the above-mentioned paint are
 immersed in deionized water at 40°C for 500 hrs.
 45 After left standing for 24 hrs, they are scribed to
 one hundred 1 mm squares, over which tape-peeling
 test is done and remaining-sound squares are counted.

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Table 2 (Continued)

5	1	Comparative Example	4	5
10	81/100 100/100 100/100	28/100 36/100 62/100	76/100 100/100 100/100	95/100 98/100 100/100
15	4 mm 4 mm 12 mm	15 mm 16 mm 20 mm	3 mm 4 mm 13 mm	2 mm 4 mm 10 mm
20	120 ppm 0.1 g/m ² 2 mg/m ² 3 mg/m ²	150 ppm 0 0 0	110 ppm 0.2 g/m ² 4 mg/m ² 5 mg/m ²	5 ppm 1.1 g/m ² 19 mg/m ² 0 5 mg/m ²
25				7 ppm 1.3 g/m ² 0 5 mg/m ²

As described above, the phosphate treatment solution for composite structures of the present invention contains predetermined amounts of Ni ions and Mn ions, and in the method for the treatment of the present invention, the content of free fluoride ions is controlled in a predetermined range. In consequence, it is possible to continuously treat even the composite structures inclusive of aluminum parts, which means that workability is improved by the present invention. In addition, the phosphate coating formed on the surfaces of the composite structures exerts the effect of improving the performance of a paint film obtained by a subsequent cathodic electrodeposition in the wet adhesion and outdoor exposure adhesion.

According to the method of the present invention, undesirable aluminum ions which are dissolved out in a continuous treatment step of the composite structures inclusive of the aluminum parts are successively precipitated and removed in the form of K_2NaAlF_6 by adding a mixture of KHF_2 and $NaHF_2$. Therefore, the present invention can provide the excellent phosphate coating.

40 Claims

Claims for the following Contracting States : DE, GB, FR

1. A phosphate treatment solution for composite structures having steel, zinc-plated steel and aluminum materials which is characterized by containing 0.3-2.0 g/l of zinc ions, 0.3-4.0 g/l of nickel ions, 0.3-2.0 g/l of manganese ions, 3-10 g/l of sodium ions, 0.1-10 g/l of potassium ions, 5.0-25.0 g/l of phosphate ions, 0.11-7.0 g/l of total fluorine ions, 4.0 g/l or more of nitrate ions and 0.01-1.0 g/l of nitrite ions as main components, said treatment solution having a pH-value of 2.0-3.5, said total fluorine ions being composed of 0.1-5 g/l as fluorine of complex fluorine ions and 0.01-2 g/l of free fluoride ions.
2. A method for treating composite structures which is characterized by using an acidic treatment solution containing 0.3-2.0 g/l of zinc ions, 0.3-4.0 g/l of nickel ions, 0.3-2.0 g/l of manganese ions, 3-10 g/l of sodium ions, 0.1-10 g/l of potassium ions, 5.0-25.0 g/l of phosphate ions, 0.11-7.0 g/l of total fluorine ions, 4.0 g/l or more of nitrate ions and 0.01-1.0 g/l of nitrite ions as main components, said treatment solution having a pH-value of 2.0-3.5, said total fluorine ions being composed of 0.1-5 g/l as fluorine of complex fluorine ions and 0.01-2 g/l of free fluoride ions, while a mixture of sodium bifluoride and potassium bifluoride is used as an additive agent so as to maintain the concentration of said free fluoride ions.

3. A method for treating composite structures according to Claim 2 wherein said mixture is composed of sodium bifluoride and potassium bifluoride in a ratio of one molecule of the former to two molecules of the latter.
- 5 4. A method for treating composite structures according to claim 2 or 3 further comprising the step of applying cathodic electrodeposition coating to it.

Claims for the following Contracting State : ES

- 10 1. A method for producing a phosphate treatment solution for composite structures having steel, zinc-plated steel and aluminum materials, which is characterized by dissolving 0.3-2.0 g/l of zinc ions, 0.3-4.0 g/l of nickel ions, 0.3-2.0 g/l of manganese ions, 3-10 g/l of sodium ions, 0.1-10 g/l of potassium ions, 5.0-25.0 g/l of phosphate ions, 0.11-7.0 g/l of total fluorine ions, 4.0 g/l or more of nitrate ions and 0.01-1.0 g/l of nitrite ions as main components, said treatment solution having a pH-value of 2.0-3.5,
15 said total fluorine ions being composed of 0.1-5 g/l as fluorine of complex fluorine ions and 0.01-2 g/l of free fluoride ions.
2. A method for treating composite structures which is characterized by using an acidic treatment solution containing 0.3-2.0 g/l of zinc ions, 0.3-4.0 g/l of nickel ions, 0.3-2.0 g/l of manganese ions, 3-10 g/l of sodium ions, 0.1-10 g/l of potassium ions, 5.0-25.0 g/l of phosphate ions, 0.11-7.0 g/l of total fluorine ions, 4.0 g/l or more of nitrate ions and 0.01-1.0 g/l of nitrite ions as main components, said treatment solution having a pH-value of 2.0-3.5, said total fluorine ions being composed of 0.1-5 g/l as fluorine of complex fluorine ions and 0.01-2 g/l of free fluoride ions, while a mixture of sodium bifluoride and potassium bifluoride is used as an additive agent so as to maintain the concentration of said free fluoride ions.
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3. A method for treating composite structures according to Claim 2 wherein said mixture is composed of sodium bifluoride and potassium bifluoride in a ratio of one molecule of the former to two molecules of the latter.
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4. A method for treating composite structures according to claim 2 or 3 further comprising the step of applying cathodic electrodeposition coating to it.

Patentansprüche

35 **Patentansprüche für folgende Vertragsstaaten : DE, GB, FR**

1. Phosphatier-Behandlungslösung für Verbundbauteile mit Stahl-, galvanisch verzinkten Stahl- und Aluminium-Werkstoffen, welche dadurch gekennzeichnet ist, daß sie
40 0,3 bis 2,0 g/l Zink-Ionen, 0,3 bis 4,0 g/l Nickel-Ionen, 0,3 bis 2,0 g/l Mangan-Ionen, 3 bis 10 g/l Natrium-Ionen, 0,1 bis 10 g/l Kalium-Ionen, 5,0 bis 25,0 g/l Phosphat-Ionen, 0,11 bis 7,0 g/l Gesamtsumme an Fluor-Ionen, 4,0 g/l oder mehr Nitrat-Ionen und 0,01 bis 1,0 g/l Nitrit-Ionen als Hauptkomponenten enthält, wobei die Behandlungslösung einen pH-Wert von 2,0 bis 3,5 besitzt und die Gesamtsumme an Fluor-Ionen zusammengesetzt ist aus 0,1 bis 5 g/l Fluor von Komplex-Fluor-Ionen und 0,01
45 bis 2 g/l freien Fluorid-Ionen.
2. Verfahren zur Behandlung von Verbundbauteilen, welches gekennzeichnet ist durch die Verwendung einer sauren Behandlungslösung, welche
50 0,3 bis 2,0 g/l Zink-Ionen, 0,3 bis 4,0 g/l Nickel-Ionen, 0,3 bis 2,0 g/l Mangan-Ionen, 3 bis 10 g/l Natrium-Ionen, 0,1 bis 10 g/l Kalium-Ionen, 5,0 bis 25,0 g/l Phosphat-Ionen, 0,11 bis 7,0 g/l Gesamtsumme an Fluor-Ionen, 4,0 g/l oder mehr Nitrat-Ionen und 0,01 bis 1,0 g/l Nitrit-Ionen als Hauptkomponenten enthält, wobei die Behandlungslösung einen pH-Wert von 2,0 bis 3,5 besitzt und die Gesamtsumme an Fluor-Ionen zusammengesetzt ist aus 0,1 bis 5 g/l Fluor von Komplex-Fluor-Ionen und 0,01 bis 2 g/l freien Fluorid-Ionen, wobei eine Mischung aus Natriumhydrogenfluorid und Kaliumhydrogenfluorid als Zusatzstoff verwendet wird, um die Konzentration der freien Fluorid-Ionen aufrechtzuerhalten.
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3. Verfahren zur Behandlung von Verbundbauteilen gemäß Anspruch 2, wobei die genannte Mischung zusammengesetzt ist aus Natriumhydrogenfluorid und Kaliumhydrogenfluorid in einem Verhältnis von

einem Molekül des ersteren zu zwei Molekülen des letzteren.

4. Verfahren zur Behandlung von Verbundbauteilen gemäß Anspruch 2 oder 3, welches zusätzlich den Schritt des Auftragens eines Überzugs auf diese durch kathodische elektrolytische Abscheidung umfaßt.

Patentansprüche für folgenden Vertragsstaat : ES

1. Verfahren zur Herstellung einer Phosphatier-Behandlungslösung für Verbundbauteile mit Stahl-, galvanisch verzinkten Stahl- und Aluminium-Werkstoffen, welche dadurch gekennzeichnet ist, daß sie 0,3 bis 2,0 g/l Zink-Ionen, 0,3 bis 4,0 g/l Nickel-Ionen, 0,3 bis 2,0 g/l Mangan-Ionen, 3 bis 10 g/l Natrium-Ionen, 0,1 bis 10 g/l Kalium-Ionen, 5,0 bis 25,0 g/l Phosphat-Ionen, 0,11 bis 7,0 g/l Gesamtsumme an Fluor-Ionen, 4,0 g/l oder mehr Nitrat-Ionen und 0,01 bis 1,0 g/l Nitrit-Ionen als Hauptkomponenten enthält, wobei die Behandlungslösung einen pH-Wert von 2,0 bis 3,5 besitzt und die Gesamtsumme an Fluor-Ionen zusammengesetzt ist aus 0,1 bis 5 g/l Fluor von Komplex-Fluor-Ionen und 0,01 bis 2 g/l freien Fluorid-Ionen.
2. Verfahren zur Behandlung von Verbundbauteilen, welches gekennzeichnet ist durch die Verwendung einer sauren Behandlungslösung, welche 0,3 bis 2,0 g/l Zink-Ionen, 0,3 bis 4,0 g/l Nickel-Ionen, 0,3 bis 2,0 g/l Mangan-Ionen, 3 bis 10 g/l Natrium-Ionen, 0,1 bis 10 g/l Kalium-Ionen, 5,0 bis 25,0 g/l Phosphat-Ionen, 0,11 bis 7,0 g/l Gesamtsumme an Fluor-Ionen, 4,0 g/l oder mehr Nitrat-Ionen und 0,01 bis 1,0 g/l Nitrit-Ionen als Hauptkomponenten enthält, wobei die Behandlungslösung einen pH-Wert von 2,0 bis 3,5 besitzt und die Gesamtsumme an Fluor-Ionen zusammengesetzt ist aus 0,1 bis 5 g/l Fluor von Komplex-Fluor-Ionen und 0,01-2 g/l freien Fluorid-Ionen, während eine Mischung aus Natriumhydrogenfluorid und Kaliumhydrogenfluorid als Zusatzstoff verwendet wird, um die Konzentration der freien Fluorid-Ionen aufrechtzuerhalten.
3. Verfahren zur Behandlung von Verbundbauteilen gemäß Anspruch 2, wobei die genannte Mischung zusammengesetzt ist aus Natriumhydrogenfluorid und Kaliumhydrogenfluorid in einem Verhältnis von einem Molekül des ersteren zu zwei Molekülen des letzteren.
4. Verfahren zur Behandlung von Verbundbauteilen gemäß Anspruch 2 oder 3, welches zusätzlich den Schritt des Auftragens eines Überzugs auf diese durch kathodische elektrolytische Abscheidung umfaßt.

Revendications

Revendications pour les Etats contractants suivants : DE, GB, FR

1. Une solution de phosphatation pour des structures composites comportant des matériaux en acier, en acier zingué et en aluminium et qui est caractérisée par la présence de 0,3-2,0 g/l d'ions zinc, 0,3-4,0 g/l d'ions nickel, 0,3-2,0 g/l d'ions manganèse, 3-10 g/l d'ions sodium, 0,1-10 g/l d'ions potassium, 5,0-25,0 g/l d'ions phosphate, 0,11-7,0 g/l d'ions fluor totaux, 4,0 g/l ou plus d'ions nitrate et 0,01-1,0 g/l d'ions nitrite comme composants principaux, ladite solution de traitement ayant une valeur de pH comprise entre 2,0 et 3,5, lesdits ions fluor totaux étant composés de 0,1-5 g/l en fluor d'ions fluorure complexes et de 0,01-2 g/l d'ions fluorure libres.
2. Une méthode pour traiter des structures composites qui est caractérisée par l'utilisation d'une solution de traitement acide comportant 0,3-2,0 g/l d'ions zinc, 0,3-4,0 g/l d'ions nickel, 0,3-2,0 g/l d'ions manganèse, 3-10 g/l d'ions sodium, 0,1-10 g/l d'ions potassium, 5,0-25,0 g/l d'ions phosphate, 0,11-7,0 g/l d'ions fluor totaux, 4,0 g/l ou plus d'ions nitrate et 0,01-1,0 g/l d'ions nitrite comme composants principaux, ladite solution de traitement ayant une valeur de pH comprise entre 2,0 et 3,5, lesdits ions fluor totaux étant composés de 0,1-5 g/l en fluor d'ions fluorure complexes et de 0,01-2 g/l d'ions fluorure libres, en utilisant un mélange de bifluorure de sodium et de bifluorure de potassium comme additif de manière à maintenir la concentration desdits ions fluorure.
3. Une méthode pour traiter des structures composites conformément à la Revendication 2 dans laquelle ledit mélange est composé de bifluorure de sodium et de bifluorure de potassium dans une proportion

de une molécule du premier pour deux molécules du dernier.

4. Une méthode pour traiter des structures composites conformément à la Revendication 2 ou 3 comportant l'étape d'application ultérieure sur cette structure d'un revêtement par électrodéposition cathodique.

Revendications pour l'Etat contractant suivant : ES

1. Une méthode pour préparer une solution de phosphatation pour des structures composites comportant des matériaux en acier, en acier zingué et en aluminium et qui est caractérisée en ce qu'on dissout 0,3-2,0 g/l d'ions zinc, 0,3-4,0 g/l d'ions nickel, 0,3-2,0 g/l d'ions manganèse, 3-10 g/l d'ions sodium, 0,1-10 g/l d'ions potassium, 5,0-25,0 g/l d'ions phosphate, 0,11-7,0 g/l d'ions fluor totaux, 4,0 g/l ou plus d'ions nitrate et 0,01-1,0 g/l d'ions nitrite comme composants principaux, ladite solution de traitement ayant une valeur de pH comprise entre 2,0 et 3,5, lesdits ions fluor totaux étant composés de 0,1-5 g/l en fluor d'ions fluorure complexes et de 0,01-2 g/l d'ions fluorure libres.
2. Une méthode pour traiter des structures composites qui est caractérisée par l'utilisation d'une solution de traitement acide comportant 0,3-2,0 g/l d'ions zinc, 0,3-4,0 g/l d'ions nickel, 0,3-2,0 g/l d'ions manganèse, 3-10 g/l d'ions sodium, 0,1-10 g/l d'ions potassium, 5,0-25,0 g/l d'ions phosphate, 0,11-7,0 g/l d'ions fluor totaux, 4,0 g/l ou plus d'ions nitrate et 0,01-1,0 g/l d'ions nitrite comme composants principaux, ladite solution de traitement ayant une valeur de pH comprise entre 2,0 et 3,5, lesdits ions fluor totaux étant composés de 0,1-5 g/l en fluor d'ions fluorure complexes et de 0,01-2 g/l d'ions fluorure libres, en utilisant un mélange de bifluorure de sodium et de bifluorure de potassium comme additif de manière à maintenir la concentration desdits ions fluorure.
3. Une méthode pour traiter des structures composites conformément à la Revendication 2 dans laquelle ledit mélange est composé de bifluorure de sodium et de bifluorure de potassium dans une proportion de une molécule du premier pour deux molécules du dernier.
4. Une méthode pour traiter des structures composites conformément à la Revendication 2 ou 3 comportant l'étape d'application ultérieure sur cette structure d'un revêtement par électrodéposition cathodique.